PASTEURIZATION OF MILK BY THE USE OF OZONE

BY

G. C. CARNAHAN
O. A. DECELLE

ARMOUR INSTITUTE OF TECHNOLOGY

1914

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the use of ozone

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PASTEURIZATION OF MILK
BY THE USE OF OZONE.

A THESIS

Presented By

G. C. Carnahan

and

O. A. DeCelle

To The

PRESIDENT AND FACULTY

of the

ARMOUR INSTITUTE OF TECHNOLOGY.

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Having Completed The Prescribed

Course of Study

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1914

Approved:---

H. McCormack
Prof. of Chem. Eng.

L. C. Monin

H M Raymond

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Ozone, chemically designated by the symbol O_3, is generated by the action of a silent discharge of high tension electricity, in an atmosphere of oxygen, the latter being either in the form of the pure gas or more usually as oxygen diluted with the other constituents of the air.

As is indicated by the formula, ozone consists of three oxygen atoms, or it may be considered to be an oxygen molecule O_2 plus an extra oxygen atom. It is generally considered that its remarkably strong oxidizing power may be attributed to this third atom. Besides its oxidizing power, it still has a wonderful germicidal property, which, according to different authorities, may be due, either to a specific property coming from some unusual combination of the oxygen atoms, or simply to the oxidizing power.

Owing to its powerful germicidal properties, its successful commercial application to water sterilization and to the fact that experts in the chemical profession seem to be divided in the opinion as to its practicability as a

sterilizing agent for raw milk, the problem stated in the title of this thesis, namely, "The Pasteurization of Milk by the Use of Ozone" was selected for original research.

In the selection of the title it was decided that the word "pasteurization" be used instead of "sterilization" as the problem was to be considered as a search for a commercial method to displace the prevalent type of milk pasteurization, namely, that of keeping the raw milk at a temperature of 170° F. for a definite period of time.

At the outset of the attack on the problem several things were decided upon as the objects to be kept most in mind. The first of these was that all methods of procedure would be such that the milk would be kept at ordinary temperatures during the process. This was because it was the desire to see the effect of ozone itself on the milk, unaided by the application of heat, and secondly, that in order to make the method commercially available, the

milk should be treated under normal temperature.

The other things had to do with the commercial application of the methods. That is, no concentration of the gas was used which could not be duplicated in regular practice on a large scale at a reasonable cost. All different methods of treatment represented on a small scale, principles which could be applied to commercial installations.

The work was separated into three main divisions, namely, collection of data as to the effct of ozone on bacteria; its effect upon the chemical constituents and physical properties, and the effects when under different methods of contact.

The germicidal effect was determined by the customary bacteria count by means of incubation on nutrient agar in Petri dishes, counts being made on the original untreated milk and on every sample of the ozonized product.

The chemical and physical effects on the

milk were determined by making analyses on all the milk treated, quantitative tests being made for acidity, casein, lactose or milk sugar, and fat; in each case.

The methods of analysis employed in this work were all the standard commercial quantitative tests. In substance they were as follows:--

The ozone was determined by absorbtion in alkaline KI solution, the I set free by the ozone being titrated with standard N/10 $Na_2S_2O_3$ after acidification with HCl, starch being used as the indicator. The alkaline KI was made up so as to be N/5 to KI and N/5 to KOH.

The fat in the milk was determined by the standard Babcock method.

The lactose or milk sugar was made by means of the sacharimeter. By using a constant, exact weight of sample based on the specific rotary power of pure lactose, it

is possible to make the polariscope read percentage direct. A certain sample, the amount depending on the specific gravity of the milk, being added to 30cc. of mercuric iodide solution, the whole being made up to 102.4 cc. and filtered. The clear filtrate was run into the sacharimeter tube and the reading made.

The analysis of the casein was the only one that was different from the customary method. The rapid method by the use of formaldehyde being employed. This method is given in full in The Journal Of Industrial and Engineering Chemistry, Vol VI;2, page 131. It consists of taking a sample of 9 cc. of milk, making neutral with phenolthalein with alkali, then adding 2 cc. of formaldehyde, also netral to phenolthalein, and then titrating with N/10 NaOH. The number of cc. of alkali used multiplied by the factor 1.63 gives the percent of casein. The acidity was determined by making note of the amount of alkali needed to bring the milk to the neutral point in the first part of the above method.

Three specific types of apparatus were used in endeavoring to find a suitable method of exposing as much milk surface as possible to the ozonized air. These~~s~~ types differed to such an extent that it was considered advisable to group all the data and discussion pertaining to each arrangement in separate divisions.

The ozone generator, which supplied the ozone for all the work, was designed by the Held company, of this city. A description would be somewhat as follows:- One electrode consisted of a steel cylinder about an inch in diameter which was sealed in a tube under partial vacuum. This vacuum tube served the purpose of keeping the ozonized air free fromm nitrous oxides, a thing which it accomplishes successfully. The other electrode was a layer of lead foil wrapped around a tube which was open at the end, this larger was of glass and fitted over the vacuum tube leaving an air space of about three-sixteenths of an inch across which passed the silent electric

discharge and thru which was drawn the current of dry air. Both tubes were fused together at the bottom so as to make a stable piece of apparatus.

The high tension current was fed to the electrodes from either a step-up transformer or an induction coil, depending upon whether 110-volt current or storage batteries were available. The step up transformer was operated from the 110-volt D.C. lighting circuit thru a small rotary converter, constructed so as to give a variable frequency. The change in the frequency of the A.C. current supplied to the transformer varied the E.M.F. on the secondary, as thus changed the concentration of the ozonized air. The entire apparatus was mounted on a panel and equipped with suitable plugs and switches.

The first form of apparatus used to introduce the ozone from the generator into the milk was one in which the milk was teated in bulk; that is, the milk was held stationary and the ozonized air drawn in thru it. To

obtain the greatest possible contact between the ozone and milk, a fractionating column containing inverted funnels was used as the container for the milk. The air was first drawn in from the room thru a calcium chloride tower which served to remove the moisture and dust from the air and prevent it from entering the ozonizer. Upon entering the ozonizer the oxygen was partially converted to ozone. The ozonized air was then drawn in at the lower part of the fractionating column and up thru the milk, leaving at the top. It was then drawn thru a gas meter and out into the atmosphere thru a suction pump. The air circulation, as is intimated, was furnished by a suction pump or water aspirator at the end of the system, so that the entire apparatus was under a partial vacuum.

All connections between the parts of the apparatus were of aluminum and glass tubing. Joints were made by means of metal couplings packed with cotton and paraffin. It was impossible to use rubber tubing at any

point in the air line, as it was oxidized by the ozone almost immediately, thus rendering it useless. Rubber stoppers were used with a protective coating of paraffin.

Between the ozonizer and milk column was inserted a three way cock and to the third branch of this was connected two gas absorption bottles for the determination of the amount of ozone in the air being drawn thru. These bottles were connected with the main air line beyond the milk column by means of a second three way cock. Thus by proper adjustment of these two three-way cocks, the ozonized air could be sent either thru the milk column or thru the gas absorption bottles as was desired.

Several runs with this arrangement gave us the following data:-

	Concentration: parts per 1000	Ozone Applied grs. per liter. of milk.	Bacteria Count per cc.
1	--- Original --------	Milk ----	80,000
2	1.33	.322	60,000
3	1.33	.483	1,800
4	--- Original -------	Milk --	340,000
5	1.01	.218	100,000
6	--- Original -------	Milk	1,650,000
7	2.0	.455	808,000
8	2.0	.850	152,000
9	--- Original -------	Milk	250,000
10	2.2	.50	56,000
11	2.2	.72	28,000
12	2.2	.94	6,000
13	--- Original -------	Milk	11,700,000
14	2.68	.685	950,000
15	--- Original -------	Milk	120,000,000
16	1.2	.441	3,830,000
17	1.2	1.0	2,290,000

No.	% Acidity	%Casein	%Lactose	%Fat
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	2.3	4.75	3.4
5	-	2.3	4.7	2.8
6	-	2.2	4.75	3.2
7	-	2.2	4.75	2.0
8	-	2.28	4.5	2.0
9	.136	2.36	4.75	6.2
10	.146	2.28	4.75	6.0
11	.146	2.28	4.75	5.0
12	.146	2.28	4.75	4.8
13	.425	2.2	4.25	6.4
14	.425	2.2	4.25	5.8
15	.34	2.12	4.3	3.0
16	.33	2.12	4.3	2.2
17	.30	2.12	4.3	1.8

The results of the operation of this arrangement of apparatus were thoroly satisfactory with regard to the action of the ozone on the bacteria and constituents of the milk. As may be seen from the preceding data, the bacteria were reduced in number such as would correspond favorably with the results of any ordinary pasteurization methods now in use.

It may be said that the bacteria that did survive the treatment were more vigorous in action than those in the original milk as the colonies from the treated milk developed in a shorter time than those from the raw milk. However, no new colonies appeared in the media when allowed to remain in conditions favorable to growth as in the case of raw milk.

None of the constituents of the milk were affected chemically by the ozone as shown by the analyses. The main objection to the foregoing arrangement of apparatus was a mechanical difficulty which reduced the percentage of fat in the milk. This difficulty arose

from the treatment of milk in stationary bulk. The air entered the lower part of the column of milk and in passing up thru it produced a churning action which tended to separate the butter," which being the lightest of all the solids, the tendency for it to gather at the top was facilitated by the upward passage of the air thru the milk. The result, as might be anticipated, was that at the end of the treatment a considerable portion of the butter fat had separated and gathered at the top of the column, thus lowering the percentage of butter in the treated milk.

As this separation of butter was undesirable the foregoing scheme of obtaining contact between the ozone and milk was abandoned.

The second arrangement of apparatus was designed to eliminate the undesirable feature of the first set up, namely, that of churning the mass of milk to such an extent as to cause the butter to separate. In this arrangement an upright calcium chloride tower of about three inches in diameter and fourteen inches high was substituted in the place of the fractionating column. No obstructions to the passage of air thru the interior of the tower were used. The aim was to let the milk break up the bubbles of air as they passed up thru the liquid. As before the air was introduced at the bottom and drawn off at the top.

This arrangement failed in its purpose as the butter still separated and the bubbles of air passes up thru the milk in too large a size to make the contact at all efficient. Accordingly the tower was filled with pebbles of about a half inch in diameter, the remainder of the apparatus being unchanged.

The following data was obtained from the foregoing arrangement:-

	Concentration: parts per 1000	Ozone Applied grs. per liter of milk.	Bacteria Count per cc.
1	--- Original	------ Milk -	3,500,000
2	2.02	1.72	1,300,000
3	2.02	2.00	500,000

Analyses.

No.	% Acidity	% Casein	% Lactose	% Fat
1	.175	2.2	4.75	4.0
2	.175	2.2	4.75	3.2
3	.175	2.2	4.75	2.8

as is shown by the above data, the bacteria reduction was as efficient as under the first method, but the same mechanical difficulties still prevailed, the butter fat continued to separate and gather on top, consequently this scheme was abandoned after one run.

The third and final arrangement was as shown in illustrations numbers 9 and 10. The ozone was produced in the usual manner. The milk was treated while in motion, the treatment taking place in a large enclosed space filled with ozonized air which was constantly being changed. In place of the milk column of the previous arrangements, two bell jars were fitted together, foot to foot, one serving as a bottom, being inverted and supported by an iron stand. The other stood on top of this and the union between the two jars was made air tight by smearing the edges with vaseline.

The ozonized air was introduced at the top of the upper bell jar thru a tube that terminated in a funnel inside of the enclosed space. The milk was held in a separate reservoir operated on the principle of a wash bottle. The air pressure for this was supplied by a constant pressure air tank. This tank consisted of a large air chamber on top of which was an open vat of water. The water

flowed from this vat into the air chamber thru a tube extending from the bottom of the vat to the lower region of the air chamber. The water replaced the air forcing it from the top thru a connection to the milk resevoir.

The second connection from the milk resevoir, corresponding to the discharge tube of a wash bottle, was an aluminum pipe that extended thru the side of the upper bell jar and up into the interior, so that the end of the tube, which was fitted with a tip, was directly underneath the funnel thru which the freshly ozonized air entered.

When the apparatus was in action the milk entered the ozonized atmosphere by being squirted up into the inner surface of the funnel over which it spread itself and flowed down in a very thin layer. At the same time, the ozonized air entered thru the inverted funnel thus presenting a most intimate contact between the ozone and milk, and a most excellent opportunity for the ozone to accomplish its purpose, namely that of destroying the bacteria. From here

the milk dripped from the surface of the funnel, falling over 12 inches thru an atmosphere high in ozone, and collecting in the bottom of the inverted bell jar from which it was drawn at the end of the treatment.

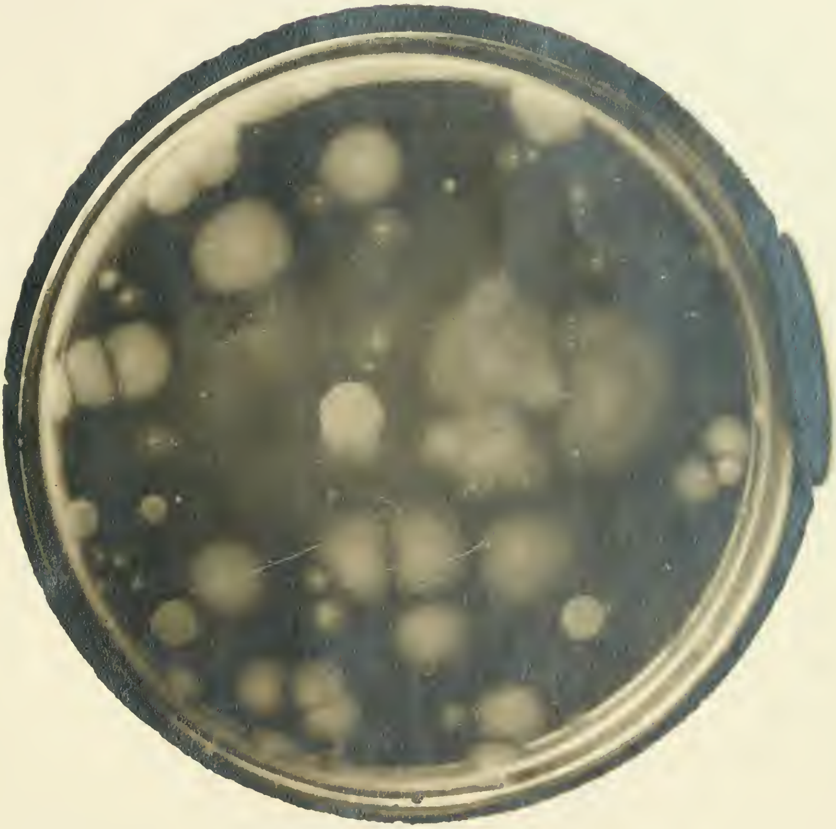
The spent ozone was drawn from the enclosed space thru the two absorption bottles by which means the excess ozone was determined. The amount of ozone that passed thru the milk and the amount absorbed by the milk were determined by the difference from the total amount of ozone passed into the system. The total ozone was determined by a period of operation in which no milk was being treated.

The following data was obtained:--

Concentration: parts per 1000		Total Ozone passed per liter milk	Ozone Absorbed per liter milk	Bacteria Count per cc.
1	---	Original --	Milk ------	37000,000
2	.8833	.0833	.07	840,000
3	.8833	.1383	.0746	250,000
4	.8833	.1933	.0776	180,000
5	---	Original --	Milk ----	280,000
6	.750	.0128	.006	180,000
7	.750	.1218	.015	105,000
8	.750	.2033	.0285	95,000
9	.750	.3123	.0535	60,000
10	---	Original --	Milk ---	7,000,000
11	1.26	.143	.007	2,150,000
12	1.26	.254	.051	290,000
13	1.26	.395	.148	120,000
14	---	Original --	Milk ---	6, 570,000
15	.079	.134	.001	4,140,000
16	.079	.302	.0705	3, 870,000
17	.079	.482	.138	1,900,000
18	.079	.672	.1722	1,500,000
19	.079	.9	.1826	1, 450,000
20	.079	1.05	.2146	1, 200,000

No.	% Acidity	%Casein	% Lactose	% Fat
1	.185	2.61	4.55	4.2
2	.18	2.6	4.4	4.1
3	.189	2.63	4.5	4.3
4	.185	2.61	4.5	4.2
5	.16	2.28	4.75	3.4
6	.162	2.3	4.7	3.38
7	.16	2.27	4.72	3.4
8	.16	2.29	4.72	3.4
9	.162	2.28	4.75	3.35
10	.365	2.20	4.5	3.8
11	.362	2.23	4.55	3.85
12	.368	2.22	4.57	3.8
13	.366	2.20	4.5	3.97
14	.275	2.36	4.6	3.5
15	.278	2.39	4.7	3.55
16	.274	2.35	4.6	3.6
17	.275	2.37	4.75	3.61
18	.277	2.39	4.7	3.6
19	.275	2.36	4.7	3.5
20	.274	2.35	4.75	3.6

PLATE ONE.



DILUTION: 1 - 1000

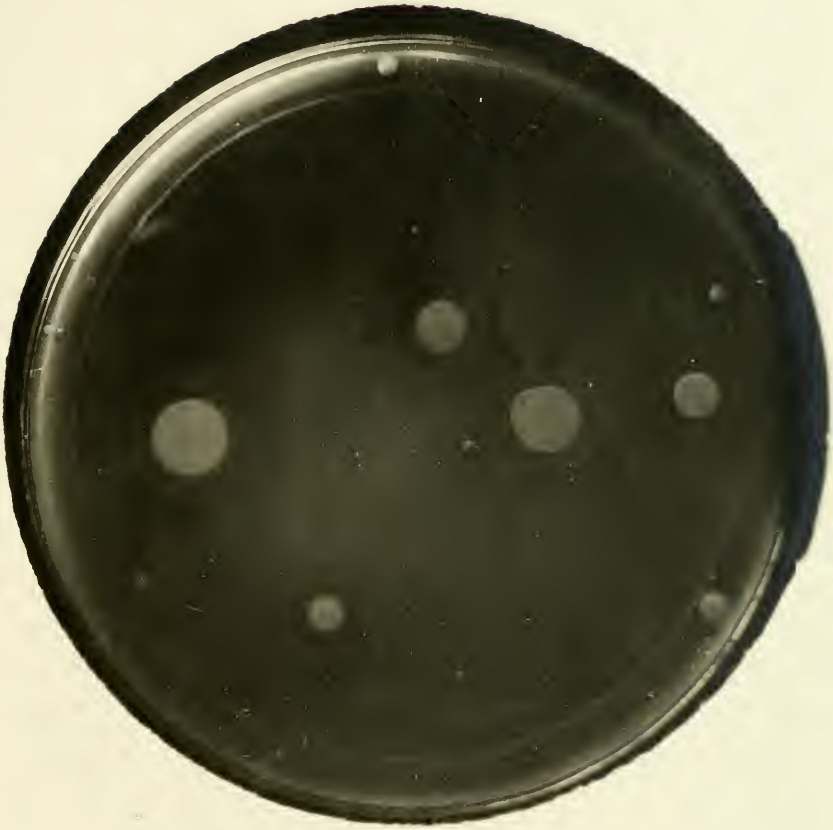
Ozone Applied : - 0.5 grs. per liter

Counts:- Original, 250,000 per cc.

Treated, 56,000 per cc.

Incubation 72 hours.

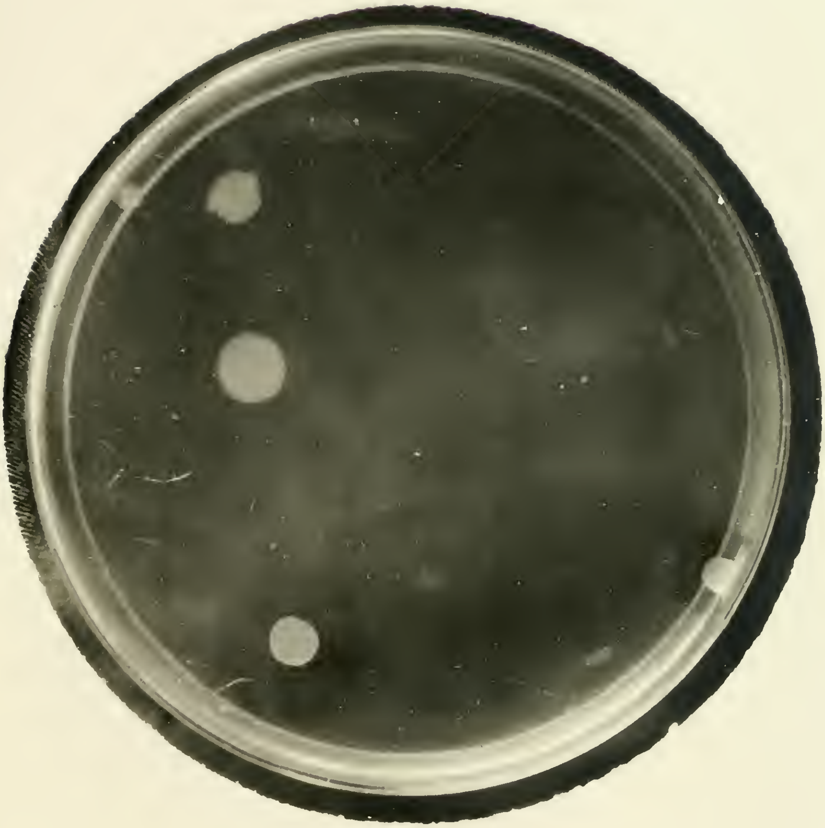
PLATE TWO.



DILUTION: 1 - 1000

Ozone Applied: - .72 grs. per liter

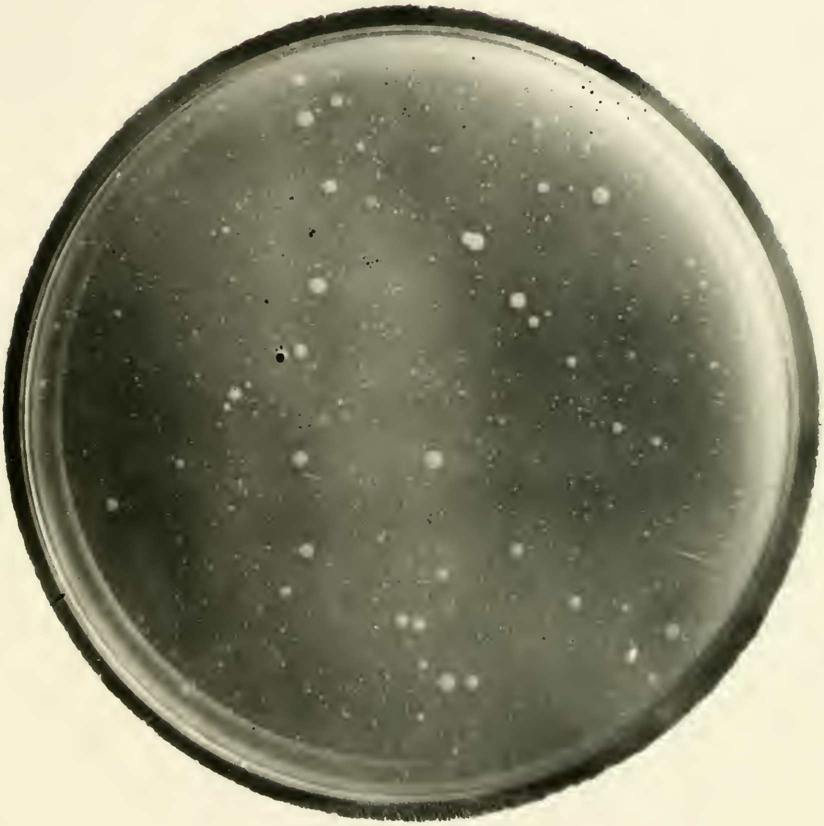
PLATE THREE.



DILUTION: 1 - 1000

Ozone Applied: - 0.94 grs. per liter

PLATE FOUR - A.

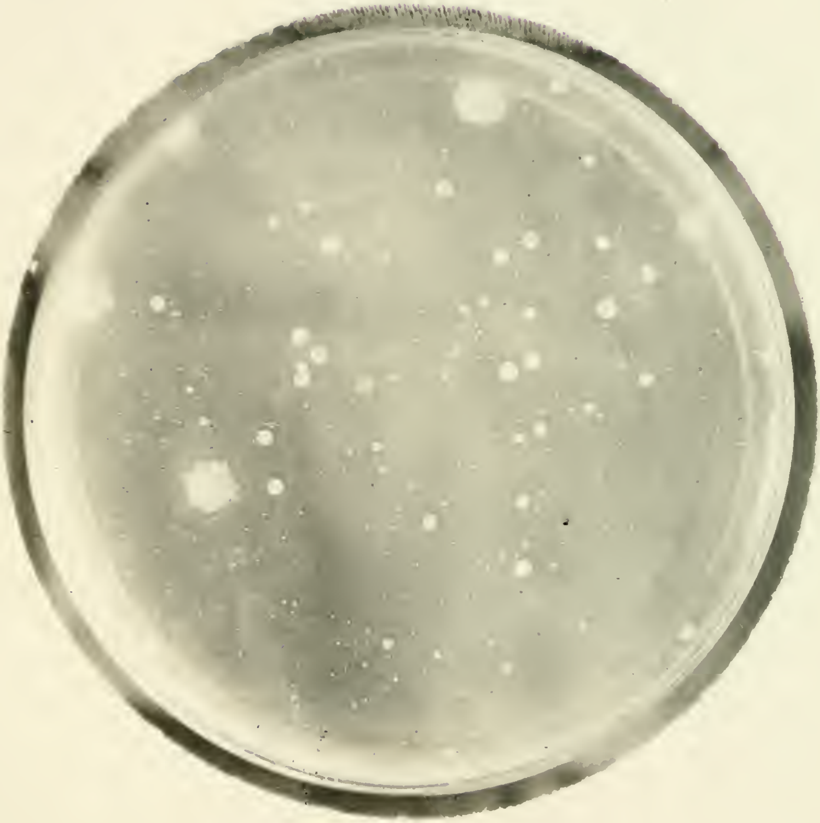


ORIGINAL MILK.

Dilution:- 1 - 10,000

Time of Incubation : 48 Hours.

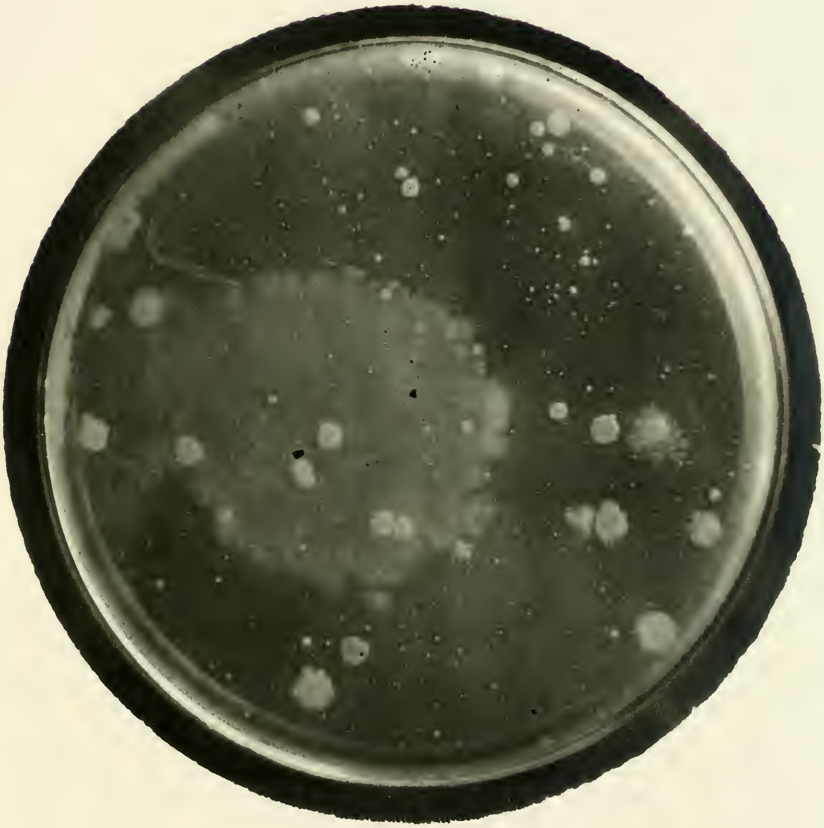
PLATE FOUR - B.



DILUTION : 1 - 10,000

Ozone Absorbed : 0.001 grs. per liter.

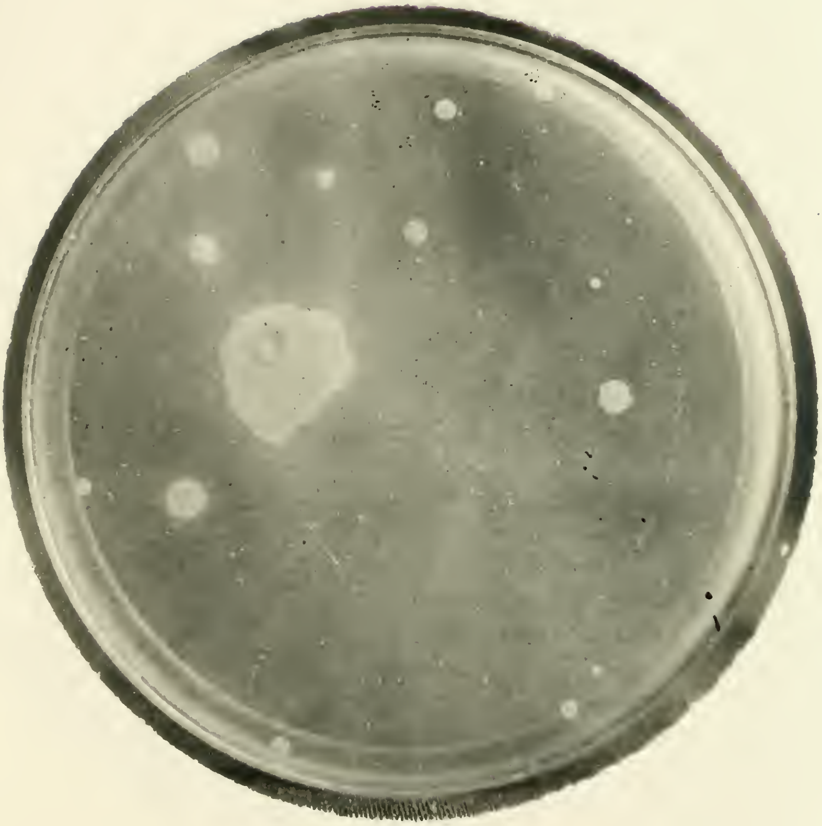
PLATE FOUR - C.



DILUTION: 1 - 10,000

Ozone Absorbed : 0.0706 grs. per liter.

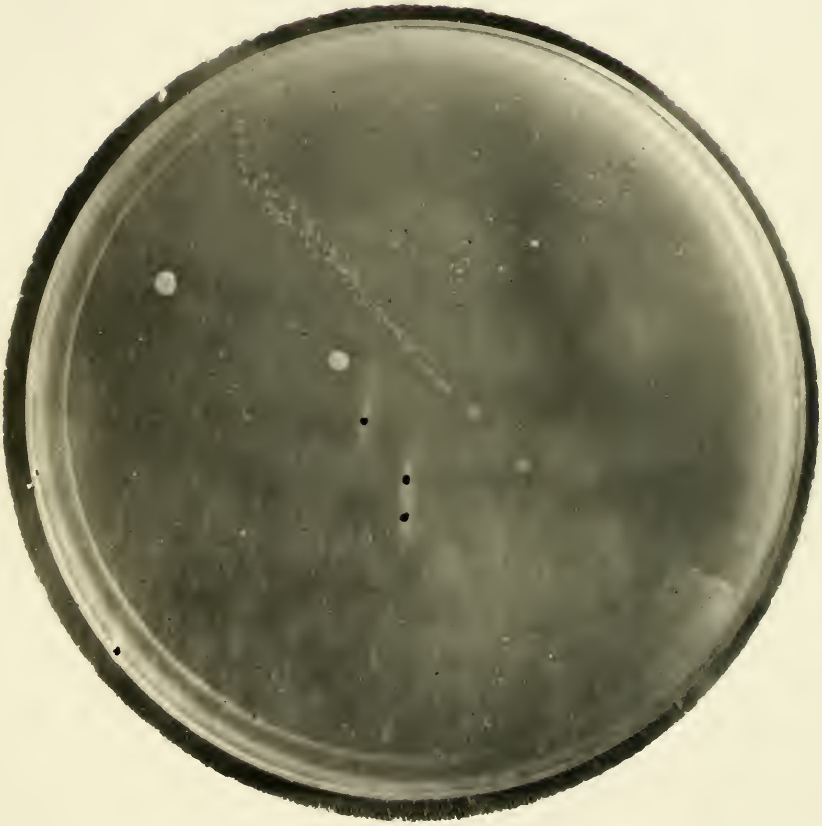
PLATE FOUR - D.



DILUTION; 1 - 10,000

Ozone Absorbed:- 0.1826 grs Per liter

PLATE FOUR - E.



DILUTION : 1 - 10,000

Ozone Absorbed :- 0.2146 grs. per liter

The above data and accompanying photographs indicate better than words that in the last type of apparatus success was attained on an experimental size of plant at least. The method of contact between the milk and ozone as employed, namely, that of submitting a moving film of milk to a highly concentrated ozonized atmosphere, eliminated all the previous troubles in regard to the separation of the butter fat. It also presented itself as a scheme which could easily be enlarged to a commercial scale. Another thing in its favor was the fact that a large quantity of milk could be treated in a comparitively short period of time.

A thing which was to be noted about this method was the fact that the surface tension of the milk changed decidedly as the film was exposed to the ozone. The milk lost nearly all its fluidity and passed off the edge of the funnel in a sort of a "stringy" mass. After being removed from the influence of the ozone the milk regained its former characteristics

no effects were otherwise noted on the physical properties or on the chemical constituents of the treated milk.

Plate Five.

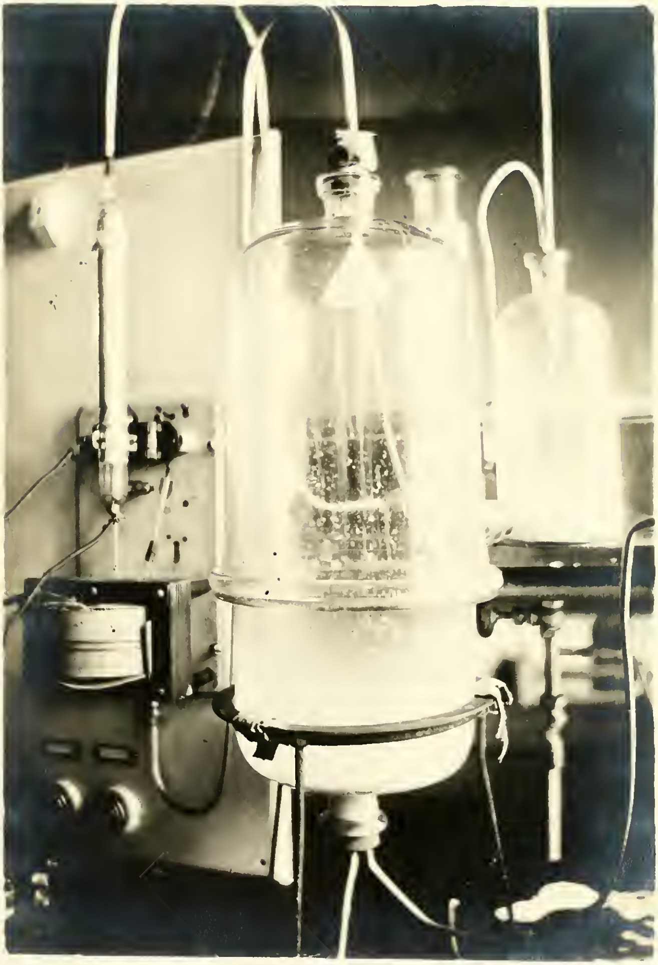
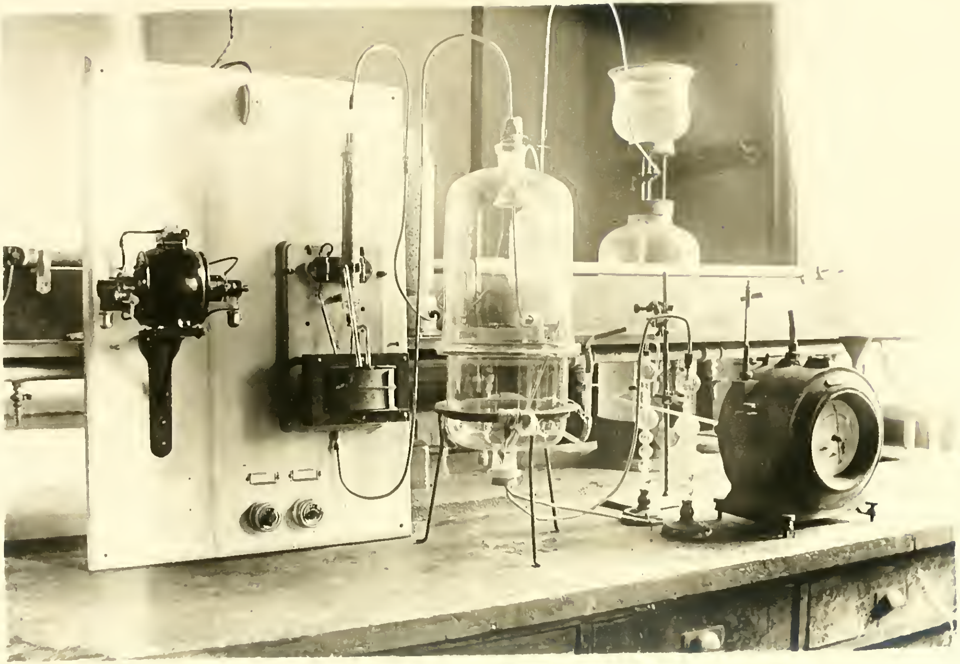


Plate Six.



The results show that ozone is an efficient germicide when applied to milk in any way. It would appear that the oxidation of the constituents which has generally been attributed to ozone, is caused by the presence of nitrous oxides with ozone. However, the late design of ozone generators which were used in this work produced no nitrous oxides, as was proven by test, and therefore, none of the oxidation of the ingredients of the milk resulted.

The extent to which the bacteria were killed and possibly the entire elimination of them by this process is evidently dependent upon the concentration of the ozone, and the length of time and method of contact.

Looking at the results from the commercial standpoint, none but the latter method presents a commercial possibility. It is the belief of the authors that by further investigation and experiment the last scheme could be developed into a practical method capable of competing successfully with the prevalent methods of pasteurizing milk..

We take this opportunity to thank Mr. Held of the Held Company for his most grateful help in furnishing us with all the necessary apparatus needed in the preparation of the ozone.

Thanks are also due to Professor Harry C. McCormack for his advice and suggestions, and also to Alfred Ernest Dean, Curator, for his help during the erection of the apparatus.

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